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전기분무법에 의해 제조되는 미립자의 형상 제어

Controlled Morphology of Particles Prepared by Electrospray Technique

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Abstract

Various structures of particles were prepared by electrospray technique. In this research, solid particles were formed by electrospraying a solution of ethanol containing polyvinyl and tetraethyl orthosilicate. During the electrospray process, the ethanol solvent was evaporated, resulting in the solidification of precursors, forming solid particles. Evaporation of ethanol solvent also enhanced the mass transport which facilitated the development of porous and hollow structures.

키워드 : *전기분무법, 액적, 합성 제어, 고체 미립자, 복합체*
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1. Introduction

Engineering particles with diverse morphologies is utmost important in material science since the particle morphology influences the characteristics of materials which determine their potential applications. Among various synthesis methods, electrospray has been recently developed for micro- or nano-particle production, micro- and nano-thin-film deposition, and micro- or nano-capsule formation with controlled morphology for various applications such as energy generation, filtration, biosensors and tissue engineering [1-3]. Electrospraying allowed the generation of particles in small size with high monodispersity. Balachandran et al. [4] used the electrospray method to produce zirconia in the size range of 50 - 500 μm. An increase in the applied ac frequency resulted in an increased rate of droplet generation, and in reduced droplet diameter and thus the smaller particles were obtained. Yun et al. [5] produced monodispersed microsphere nanoparticle-polymer TiO_2-PMMA composites with mean diameters in the size range of 0.25-1.87μm. They found that nonagglomerated TiO_2 nanoparticles were highly dispersed inside the polymer matrices. The particle size was controlled by adjusting the concentration ratio of TiO_2 to polymer in the precursor. Recently, Hwang et al. [6] utilized the electrospray technique to prepare hierarchically structured TiO_2 spheres for photoelectrodes of highly efficient dye-sensitized solar cells. The TiO_2 spheres with diameter of about 640nm were prepared by spraying a colloidal solution of

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TiO_2 nanoparticles dispersed in ethanol. The photoelectrode for dye-sensitized solar cells was produced by deposition of thoses pheres onto FTO substrate. This preparation procedure possessed several advantages such as good adhesion between the TiO_2 layer and the substrate, binder-free and low-cost process by eliminating hydrothermal treatment of electrode.

Nano- and micro-structured particles from organic materials were also produced by electrospray technique for biotechnological purposes. It has been found that the electrospraying technique is very simple to operate and can produce particles without disturbing the physical and chemical stability of the drug. For example, antibodies were electrosprayed to form particles of diameter of 130 - 350 mm and remained biologically active after this process [7]. Uematsu et al. [8] prepared biologically active proteins (α -lactalbumina) for protein-based biomaterials, biosensors, and biochips with fine porous structure, having pores in the size range 40 - 600 nm. Characteristics of products were unaffected by the high potential used for electrospraying. Wu et al. [9] demonstrated the fabrication of elastin-like polypeptides (ELP) particles for drug delivery through electrospraying. Higher flow rates and lower spraying voltages resulted in the formation of particles with tail structures and fibers along with spherical particles. They evaluated the encapsulation and triggered release of a model drug, Dox, from ELP particles and observed that the release of Dox from pH responsive particles followed the pH-dependent solubility of the ELP.

With the advantage of uniform particles generation, advances in the electrospraying technology will certainly continue in near future. In our research, nanostructures were obtained by electrospraying a solution of polyvinyl pyrrolydone (PVP) and tetraethyl orthosilicate (TEOS). The effects of feed rate and PVP content on the development of product particle structures were analyzed.

2. Experiment

Polyvinyl pyrrolydone (PVP, Sigma, M_W=55000) and tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 98%) were used as precursors. In a typical experiment, PVP was dissolved in 8 mL ethanol solution (Deajung, 99.9%), followed by addition of 2mL TEOS. The precursors were well mixed to obtain a homogeneous precursor solution.

Fig. 1 shows a schematic the illustration of electrospraying setup. The electrospraying setup consisted of a syringe pump which loaded with a syringe, a high-voltage supply and a counter electrode as ground collector. In our experiments, the precursor solution was loaded into a glass syringe which equipped with a 21-gauge stainless-steel needle and was continuously sprayed by the syringe pump. The stainless-steel needle of syringe pump was connected to the high-voltage supply. The applied potential was maintained at 15 kV. The distance between the tip of the syringe needle and the Alumina foil collector was fixed at 15 cm. The products were collected and then characterized without further treatment. Morphologies of product particles were observed with a Hitachi S-4800 ultra-high resolution SEM equipment using a 15 kV electron beam with the resolution of 1 nm.

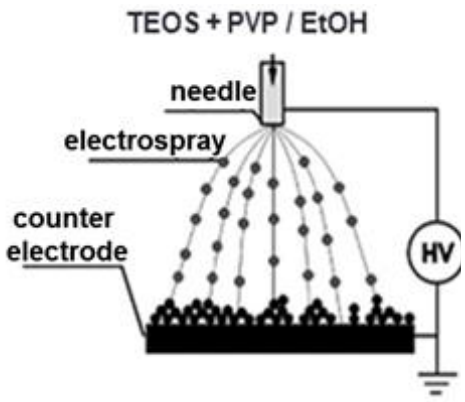

Fig 1. Schematic of electrospraying technique setup for synthesis of particles.

3. Results and Discussions

Fig. 2 shows the morphologies of electrosprayed particles obtained for different feed rates while the amount of PVP was kept at 0.5 g. As indicated in Fig. 2a, spherical particles with mean diameter of about 1 μm were obtained for feed rate of 0.5 mL/hr. When

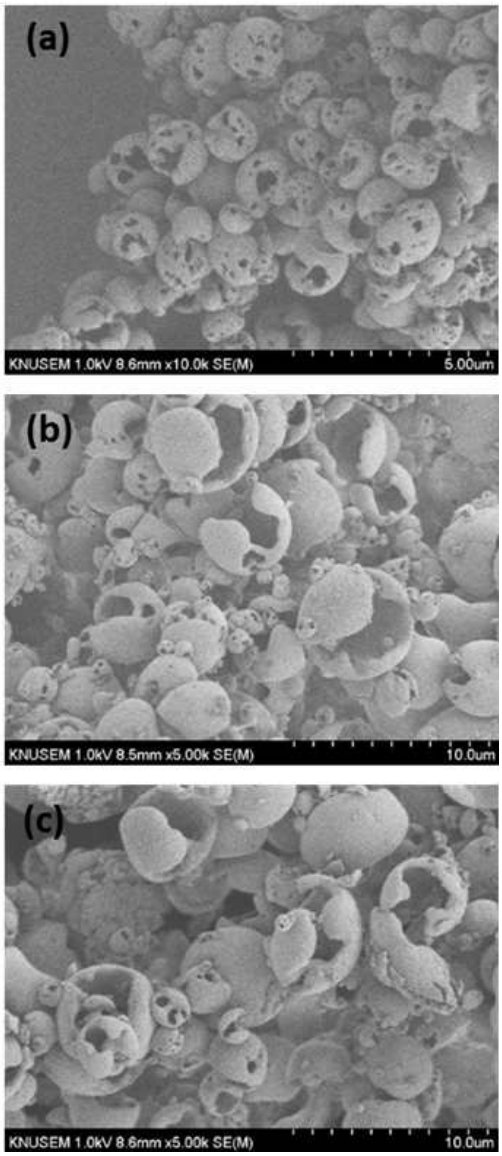

Fig. 2. SEM images of particles prepared for different feed rates (a) 0.5 mL/hr (b) 2 mL/hr and (c) 5 mL/hr.

the feed rate for precursor solution increased to 2 mL/hr and 5 mL/hr, the particles were obtained with broad size distribution, ranging from 1 μm to over 5 μm. In our process, the precursor solution flowing out from a capillary nozzle maintained at high potential was subjected to an electric field. The electric field caused elongation of the meniscus of highly charged solution to form a jet. The jet deformed and disrupted into droplets due mainly to electrical force. The solvent evaporation led to shrinkage of droplet and increase of charge intensity. At a given radius, the increasing repulsion between the charges overcame the surface tension at the droplet surface and caused a Coulomb explosion of the droplet which resulted in generation of fine droplets. Faster feed rate of precursor solution caused faster movement of droplets which would reduce the breakage of droplets by Coulomb explosion and thus resulted in generation of larger particles.

Observation of particle morphology from SEM analysis indicated that the solid particles exhibited solid shell and empty core structure. It should be noticed that, during moving downfield through the air toward the counter electrode, the ethanol solvent from the electrosprayed droplets could evaporate and thus the remaining precursors would solidify to form solid particles. The solidification of precursors could take place initially on the surface of droplets, forming a stable solid shell. Continuous evaporation of ethanol facilitated mass transport of precursor from the core to the solid shell which induced the formation of hollow core structure. However, since the hollow core structure was formed with complete depletion of core materials, there would be a negative pressure at the hollow core. The ambient air might rush into the hollow core which resulted in the formation of breakage on the solid shell.

Fig 3 shows the SEM image of particles prepared for 2 g of PVP with feed rate of 2 mL/hr and the energy-dispersive X-ray spectroscopy (EDS) spectra of these particles. The particles were obtained with diameter ranging from 1 μm to over 5 μm without breakage or holes on the surfaces. As the PVP amount increased, the solid shell became more stable and thus the spherical structure was dented rather than was broken due to the pressure difference between inner core and surrounding atmosphere. The SEM image exhibited formation of individual solid particles. No adhesion between particles was clearly observed. The absence of agglomeration and coagulation of product particles indicated that

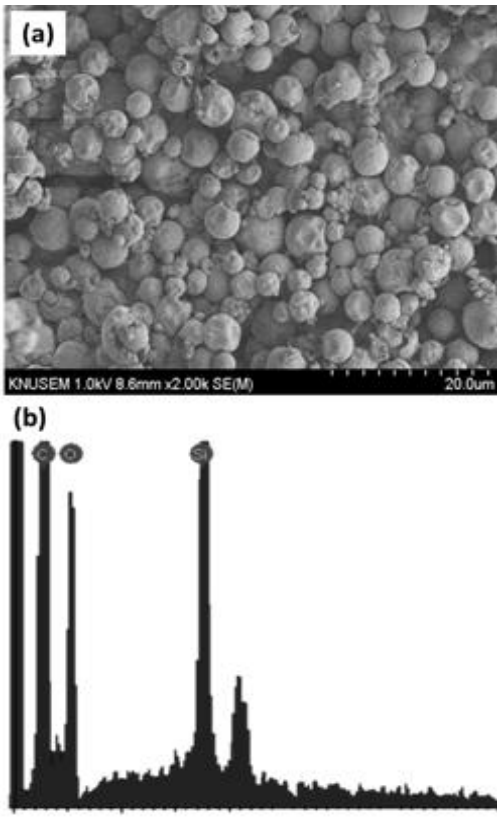

Fig.3. (a) SEM image of particles prepared for 2g of PVP and (b) corresponding energy-dispersive X-ray spectroscopy (EDS) spectra of the product particles.

the charged droplets were self-dispersing in the air and were completely transformed into solid during moving downfield through the air toward the collector. As shown in Fig. 3b, the energy-dispersive X-ray spectroscopy (EDS) spectra of these particles were obtained to further investigate the component of prepared particles. The elements detected by EDS largely comprised C, O, and Si. This result was consistent with the composition of the precursor used for electrospray, indicating the formation of composite material. This investigation could be considered as an interesting demonstration for polymer encapsulation of a colloidal suspension.

4. Conclusion

We have demonstrated that the electrospray technique could be used to prepare the particles with controlled morphology. By adjusting the PVP amount in precursor solution, broken spheres and dented spheres were obtained. The evaporation of ethanol during the electrospray process induced the solidification of precursors, resulted in formation of solid particles. The continuous evaporation of ethanol facilitated the mass transport of precursors from the core to the solid shell which led to the formation of hollow core and porous structures.

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